Enhanced High Temperature Performance of NOx Storage/Reduction (NSR) Materials

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Project Overview

Timeline
• Start – July 2009
• Finish – July 2012
• 20% complete

Budget
• Total project funding
  • DOE: ~$1,000K
  • Matched 50/50 by Cummins as per CRADA agreement
• DOE funding received in FY09:
  • $200K

Barriers
• Discussed on next slide

Partners
• Pacific Northwest National Laboratory
• Cummins, Inc.
  • w/Johnson Matthey
• In looking forward to 2012 and beyond with expected more stringent regulations, a critical need for future NSR systems will be significantly improved higher temperature performance and stability. For example, current NSR catalyst formulations are not effective for NOx removal during high temperature system maintenance events including desulfation.

• It is important to reduce system costs by, for example, minimizing the precious metal content while maintaining, even improving, performance and long-term stability.
Focus of New CRADA

Higher Temperature Lean NOx Performance:

- Better NOx storage at higher temperatures
  - Modify the NSR storage and/or support material to expand NOx trapping at higher temperatures?
  - Improved NOx storage means enhanced SOx stability – enhance thermal stability to higher temperature deSOx?
- Develop selectivity to NOx over SOx?
- Do something else at higher temperature for lean NOx removal rather than trapping?
Goals and Objectives

• Develop a fundamental understanding of candidate next generation NSR materials operated at high temperatures for NOx after-treatment for light-duty lean-burn (including diesel) engines.

• Focus on characterizing and understanding the following specific issues:
  – the various roles for the precious metals;
  – the effects of high temperatures on the precious metal and storage elements in their various roles;
  – mechanisms for higher temperature NOx storage performance for modified and/or alternative storage materials;
  – the sulfur adsorption and regeneration mechanisms for modified and/or alternative storage materials.
Approach

- Prepare and Process High Temperature NSR Materials
  - Fully formulated catalyst has been provided by Johnson Matthey.
  - PNNL is preparing model HT NSR catalysts, including changes to the storage element and support material.
  - These materials are studied:
    - Fresh, as-received (AR)
    - Variably sulfated (including engine-aged)

- Utilize expertise and state-of-the-art catalyst characterization and testing facilities at PNNL’s IIC to address mechanisms and structure/function
  - XRD, XPS, NMR, TEM/EDX and SEM/EDX
  - NO$_2$ TPD, H$_2$ TPRX
  - Lab reaction systems
  - Synchrotron based techniques (XANES, EXAFS, and in situ time-resolved XRD)
Collaborations/Interactions

- Provide results of current performance testing of NOx adsorber systems
- Carry out and disseminate results of mechanistic studies using catalyst characterization and testing
- Engine dynamometer testing of new formulations.
- Synchrotron-based in situ experiment
- Supply catalyst materials, and provide information on their preparation and initial characterization

- Conference calls are typically held once every month or two to discuss the results.
- Annual face to face CRADA review will be held in Detroit this September during the DEER meeting.
Three Initial Areas of Focus

• A quick survey of high temperature DeNOx catalysts
  – Candidates and limitations

• Fully formulated high temperature NSR catalysts supplied from Johnson Matthey.
  – As a baseline for comparison with model catalysts, NSR performance of fresh samples as a function of temperature is measured.
  – The effects of thermal aging and sulfation/desulfation on the NOx storage activity of these materials is being determined.

• High temperature NSR catalysts prepared by PNNL
  – Examine the effects of storage elements and various supports on the NOx storage activity, while screening catalyst activity behavior.
  – Determine the mechanisms of NOx storage on the high temperature storage materials.
NO decomposition, perhaps the most ideal process for removing NOx at high temperature, was surveyed. However, even recently reported materials were found to have impractically low activity.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conditions</th>
<th>Author</th>
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</thead>
<tbody>
<tr>
<td>BaO/MgO</td>
<td>1% NO, 0.2 g, 40 cc/min</td>
<td>Lunsford (Texas A&amp;M)</td>
</tr>
<tr>
<td>((\text{Gd}<em>{0.7}\text{Y}</em>{0.26}\text{Ba}<em>{0.04})\text{O}</em>{2.96})</td>
<td>1% NO, 1g, 20 cc/min</td>
<td>Imanaka (Osaka)</td>
</tr>
<tr>
<td>(\text{La}<em>{0.7}\text{Ba}</em>{0.3}\text{Mn}<em>{0.8}\text{In}</em>{0.2}\text{O}_3)</td>
<td>1% NO, 1g, 20 cc/min</td>
<td>Ishihara (Kyushu)</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.8}\text{La}</em>{0.2}\text{Mn}<em>{0.8}\text{Mg}</em>{0.2}\text{O}_3)</td>
<td>1% NO, 1g, 20 cc/min</td>
<td>Ishihara (Kyushu)</td>
</tr>
<tr>
<td>(\text{La}<em>{1.2}\text{Ba}</em>{0.8}\text{NiO}_4)</td>
<td>4% NO, 0.5g, 25 cc/min</td>
<td>Yuan (Heilongjiang)</td>
</tr>
</tbody>
</table>

- Impractical reaction condition: too low Space velocity
- Strong inhibition by \(\text{O}_2\): not applicable for lean condition
- Quite low activity up to 700 °C
- Low surface area of the mixed oxides (<10 m²/g)
As a baseline study to compare more recently published formulations, BaO/MgO catalysts, known to have good NO decomposition activity, were studied. In fact, while these were the best materials in our hands, their performance seems too low for practical application.

20wt% BaO/MgO
0.2 g, 0.5% NO, 35 cc/min

Negligible activity (<2%) at high SV
300 ppm NO with 100 cc/min
→ Low intrinsic activity
Three Initial Areas of Focus

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The sample supplied from JM shows highest activities between 400 and 450 °C. The sample was also tested after aging at elevated temperatures to understand its thermal stability.

Note: NOx uptake = total NOx uptake up to the 20% of NOx conc.
The NOx storage performance of the JM sample monotonically decreased with increasing exposure to SO$_2$. 
NOx uptake increased after desulfation at 600 ºC due to sulfur removal. However, performance monotonically decreased for desulfations above 700 ºC due to dominant thermal aging effects. Further studies will address optimum regeneration conditions.
Three Initial Areas of Focus

• **A quick survey of high temperature DeNOx catalysts**
  – Candidates and limitations

• **Fully formulated high temperature NSR catalysts supplied from Johnson Matthey.**
  – As a baseline for comparison with model catalysts, NSR performance of fresh samples as a function of temperature is measured.
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• **High temperature NSR catalysts prepared by PNNL (including model materials relevant to JM formulation – won’t discuss these).**
  – Examine the effects of storage elements and various supports on the NOx storage activity, while screening catalyst activity behavior.
  – Determine the mechanisms of NOx storage on the high temperature storage materials.
NSR catalysts with varied storage element (K) and supports giving HT storage ability have been reported. For example, our results, shown below, indicate that NO storage ability can be improved by changing the support material from $\text{Al}_2\text{O}_3$ to $\text{MgAl}_2\text{O}_4$. 

![Graph showing absorption capacity and NOx level over temperature and time for Al$_2$O$_3$ and MgAl$_2$O$_4$ supports.](attachment:chart.png)
Toyota-published high temperature NSR catalyst

New approach to enhance the NOx storage performance at high temperature using basic MgAl2O4 spinel support

Naoki Takahashi *, Shin’ichi Matsunaga, Toshiyuki Tanaka, Hideo Sobukawa, Hirofumi Shinjoh

* At 600 °C

• K/Pt/MgAl2O4 catalyst
• Durability (SO2) not addressed in the paper
When K is used as a storage element, the temperature where NOx uptake is maximized shifted to 350 - 400 ºC. The following graph clearly shows the importance of support material for higher NOx uptake.

Further studies (K loading, other support, sulfur effect) are in progress.
Proposed Future Work

1. Preparation and characterization of High temperature NSR materials at PNNL
   - Activity measurement screening of candidate samples.
   - Fundamental understanding of the behavior of K as a NOx storage element, especially related to its mobility at high temperatures.
   - Investigating NSR support effects, especially with respect to the chemistry of nitrates and sulfates at high temperature.

2. Characterization of high temperature NSR materials supplied from JM
   - Providing information about thermal stability of the catalyst.
   - Understanding sulfation/desulfation behavior.
   - Determining optimum conditions for effective regeneration with minimized degradation.
Summary

- A critical need for future NSR systems will be significantly improved **higher temperature performance** and stability, since current NSR systems are not effective during high temperature system maintenance events.

- PNNL’s role is to prepare and characterize model NSR materials that show promise for higher temperature performance, and to provide fundamental insights into specific issues concerning HT NSR catalysts identified from Cummins’ and JM’s experiences during system development.

- Technical highlights from this project this year include:
  - Preparation and evaluation of candidate materials for HT DeNOx, with a specific focus now on HT NSR catalysts.
  - Initial evaluations of HT NSR materials supplied from JM were obtained as a baseline, and durability issues of thermal aging and sulfation/desulfation are now being addressed.